

Lecture 5.

Basics of gaseous absorption/emission. Line shapes.

Objectives:

1. Basics of atomic and molecular absorption/emission spectra.
2. Spectral line shapes: Lorentz profile, Doppler profile and Voigt profile

Required reading:

L02: 1.3

Recommended/advanced reading:

G&Y: 3, 5

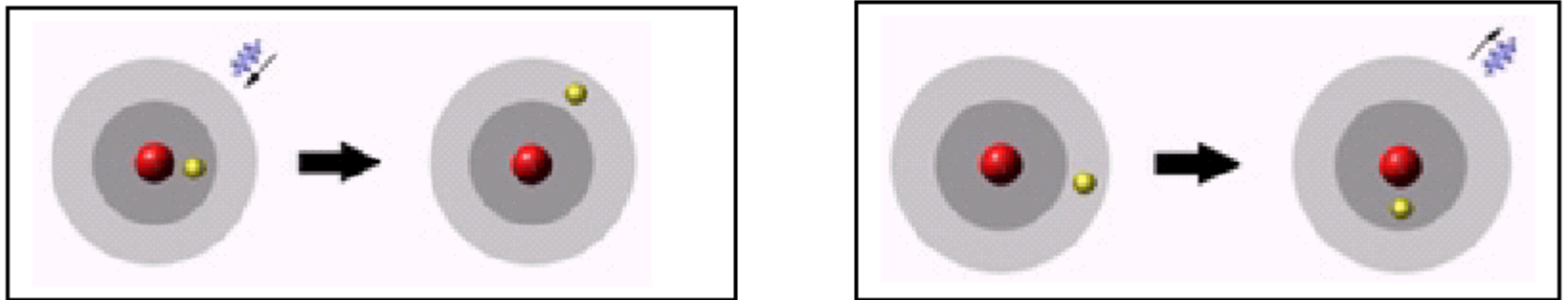
McCartney, E.J., Absorption and emission by atmospheric gases. John Wiley&Sons, 1983.

1. Basics of atomic and molecular absorption/emission spectra

Quantum mechanics governs interaction of light and single molecules.

Absorption of a photon is due to a transition to a higher quantized energy level in an atom or molecule.

Figure 6. 1 Absorption/Emission processes



Atomic absorption/emission spectra.

- Radiation emission (absorption) occurs only when an electron makes a transition from one state with energy E_k to a state with lower (higher) energy E_j :

$$\text{for emission: } E_k - E_j = h\nu$$

$\Delta E = h\tilde{\nu} = h\nu = hc/\lambda$ where $h = 6.626 \times 10^{-34} \text{ J s}$ is Planck's constant.

Bohr's model of a hydrogen atom:

- The energy level is given as

$$E_n = -\frac{R_H hc}{n^2}, n=1,2,3,\dots \quad [6.1]$$

where R_H is the Ryberg constant ($=1.092 \times 10^5 \text{ cm}^{-1}$ for hydrogen); h is the Planck's constant, and c is the speed of light.

- The wavenumber of emission/absorption lines of hydrogen atom:

$$\nu = R_H \left(\frac{1}{j^2} - \frac{1}{k^2} \right) \quad [6.2]$$

where j and k are integers defining the lower and higher energy levels, respectively.

Figure 6.2 Energy level diagram for the hydrogen atom.

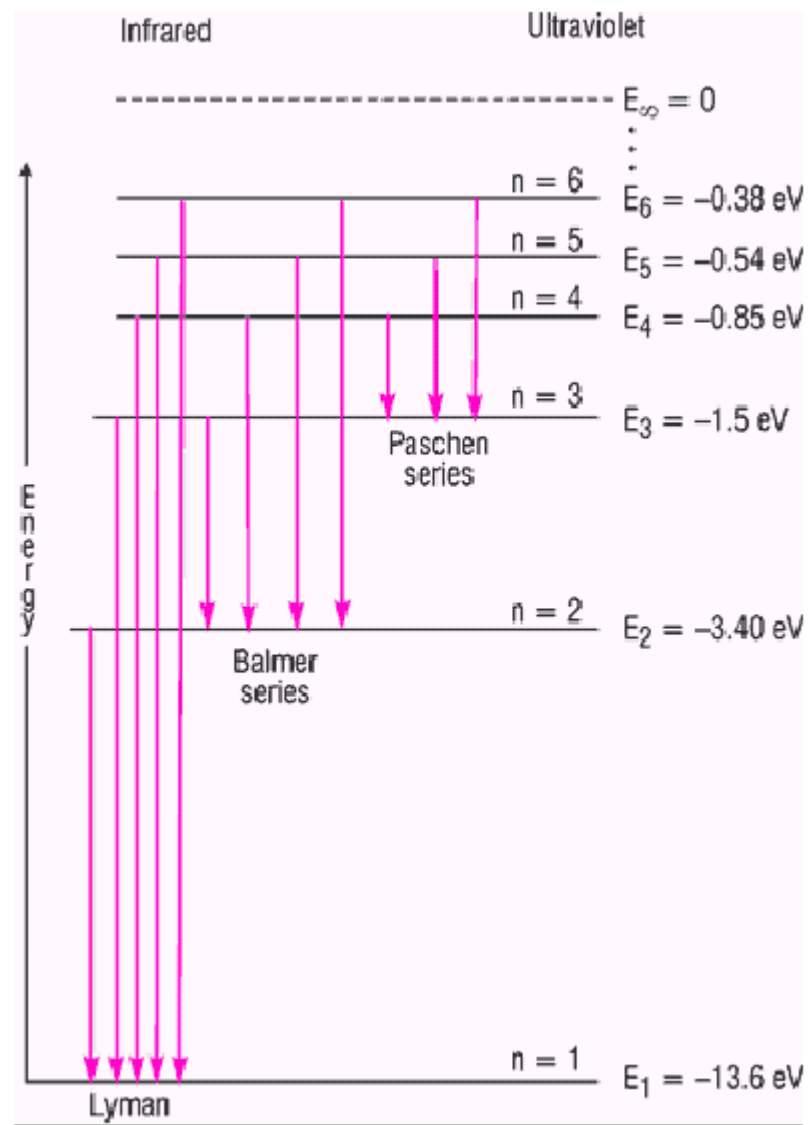
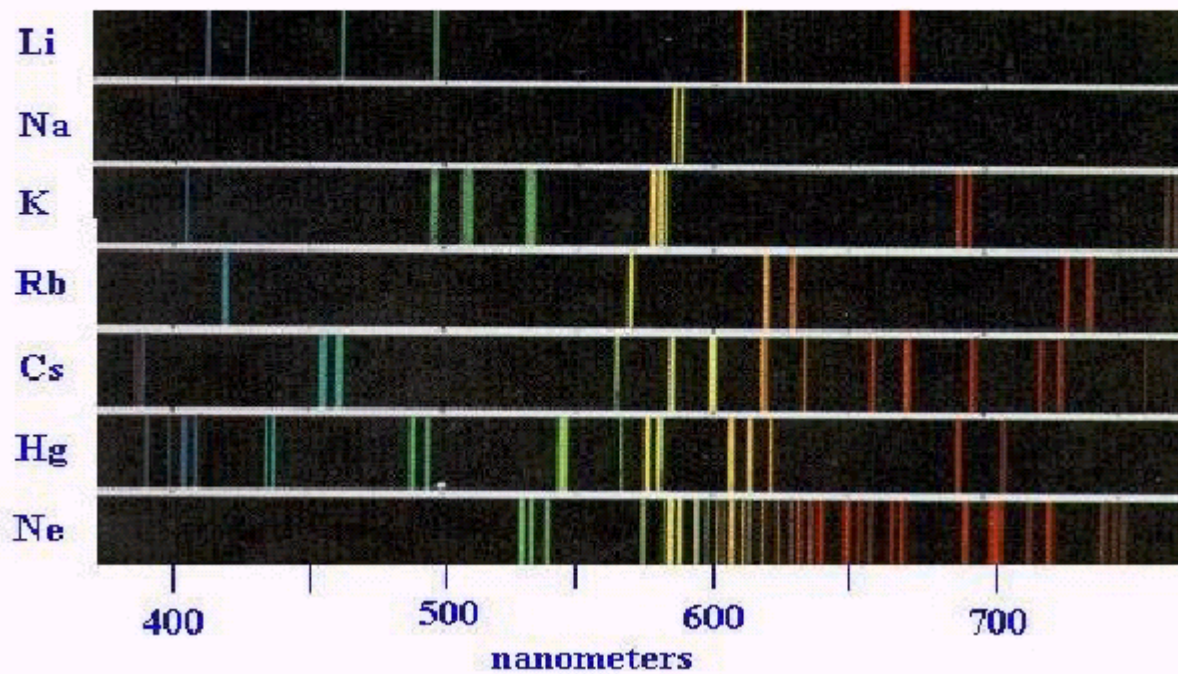


Figure 6.3 Examples of atomic spectra.

Black Body



Molecular absorption/emission spectra.

Molecular absorption spectrum is substantially more complicated than that of an atom because molecules have several forms of internal energy. This is the subject of **spectroscopy** and **quantum theory**.

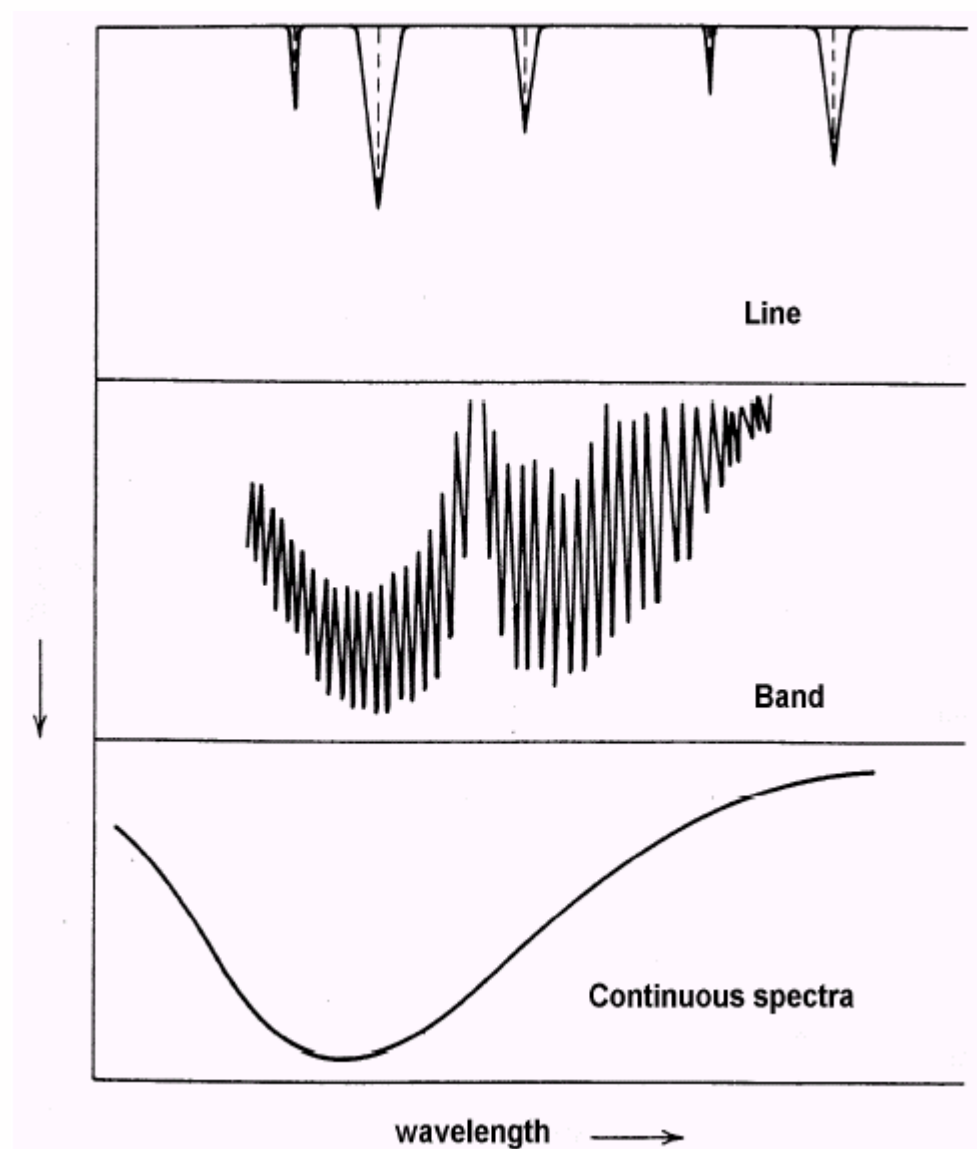
Three types of absorption/emission spectra:

- i) Sharp **lines** of finite widths
- ii) Aggregations (series) of lines called **bands**;
- iii) **Spectral continuum** extending over a broad range of wavelengths

The structure of molecules is important for an understanding of their energy forms:

- ✓ Linear molecules (CO_2 , N_2O ; C_2H_2 , all diatomic molecules):
- ✓ Symmetric top molecules (NH_3 , CH_3Cl , CF_3Cl)
- ✓ Spherical symmetric top molecules (CH_4)
- ✓ Asymmetric top molecules (H_2O , O_3)

Figure 6.4 Concept of a line, band, and continuous spectra



Main underlying principles of molecular absorption/emission.:

1) The origins of absorption/emission lie in exchanges of energy between gas molecules and electromagnetic field.

2) In general, total energy of a molecule can be given as:

$$E = E_{\text{rot}} + E_{\text{vib}} + E_{\text{el}} + E_{\text{tr}}$$

E_{rot} is the kinetic energy of rotation (energy of the rotation of a molecule as a unit body): about $1\text{-}500\text{ cm}^{-1}$ (far-infrared to microwave region)

E_{vib} is the kinetic energy of vibration: energy of vibrating nuclei about their equilibrium positions; about $500\text{ to }10^4\text{ cm}^{-1}$ (near- to far-IR)

E_{el} is the electronic energy: potential energy of electron arrangement; about $10^4\text{-}10^5\text{ cm}^{-1}$ (UV and visible)

E_{tr} is translation energy: exchange of kinetic energy between the molecules during collisions; about 400 cm^{-1} for $T = 300\text{ K}$

- From $E_{\text{rot}} < E_{\text{tr}} < E_{\text{vib}} < E_{\text{el}}$ follows that:

- Rotational energy change will accompany a vibrational transition. Therefore, vibration-rotation bands are often formed.
- Kinetic collision, by changing the translation energy, influence rotational levels strongly, vibrational levels slightly, and electronic levels scarcely at all.
























- Energy E_{rot} , E_{vib} , and E_{el} are quantized and have only discrete values specified by one or more **quantum numbers** (see below). Not all transitions between quantized energy level are allowed - they are subject to selection rules.

3) Radiative transitions of purely **rotational energy** require that a molecule possess a permanent electrical or magnetic **dipole moment**.

Species	Pure rotation lines
H ₂ O, O ₃	microwave and far IR
O ₂	microwave (weak, from permanent magnetic dipole)
CO ₂ , N ₂	none

NOTE: A **dipole** is represented by centers of positive and negative charges Q separated by a distance d : the **dipole moment** = $Q d$

Table 6.1 Atmospheric molecule structure and dipole moment status.

Molecule	Structure	Permanent dipole moment	May acquire dipole moment
N ₂	N  —  N	No	No
O ₂	O  —  O	No	No
CO	C  —  O	Yes	Yes
CO ₂	O  —  C —  O	No	Yes (in two vibrational modes)
N ₂ O	N  —  N —  O	Yes	Yes
H ₂ O	 H —  O —  H	Yes	Yes
O ₃	 O —  O —  O	Yes	Yes
CH ₄	 H —  C —  H  H —  H	No	Yes (in two vibrational modes)

NOTE: If charges are distributed symmetrically => no permanent dipole moment => no radiative activity in the far-infrared (i.e., no transitions in rotational energy)

Example: homonuclear diatomic molecules (N_2 , O_2);

NOTE: CO_2 and CH_4 don't have permanent dipole moment => no pure rotational transitions. But they can acquire the oscillating dipole moments in their vibrational modes => have vibration-rotation bands

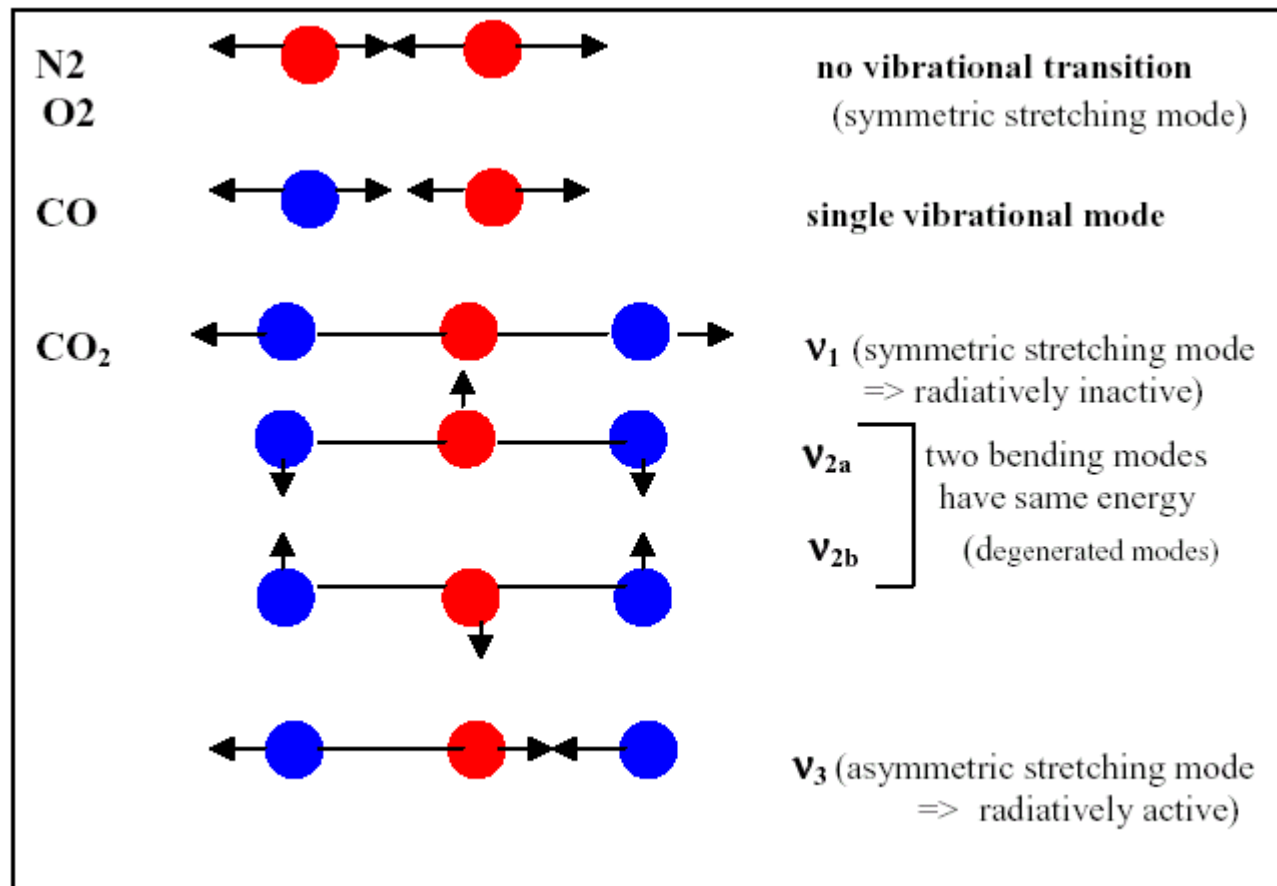
NOTE: CO , N_2O , H_2O and O_3 exhibit pure rotational spectra.

4) Radiative transitions of vibrational energy require a change in the dipole moment (i.e., oscillating moment)

Three vibrational modes of molecules:

- ν_1 symmetric stretch ($2.7 \mu\text{m}$ H_2O)
- ν_2 bending mode ($15.0 \mu\text{m}$ CO_2 , $6.3 \mu\text{m}$ H_2O)
- ν_3 asymmetric stretch ($4.3 \mu\text{m}$ CO_2 , $2.7 \mu\text{m}$ H_2O)

Figure 6.5 Vibrational modes of diatomic and triatomic atmospheric molecules.



NOTE: Homonuclear diatomic molecules N_2 and O_2 don't have neither rotational nor vibrational transitions (because of their symmetrical structures) \Rightarrow no radiative activity in the infrared. But these molecules become radiatively active in UV.

NOTE: The number of independent vibrational modes (called **normal modes**) of a molecule with $N > 2$ atoms are $3N - 6$ for non-linear molecules and $3N - 5$ for a linear molecule.

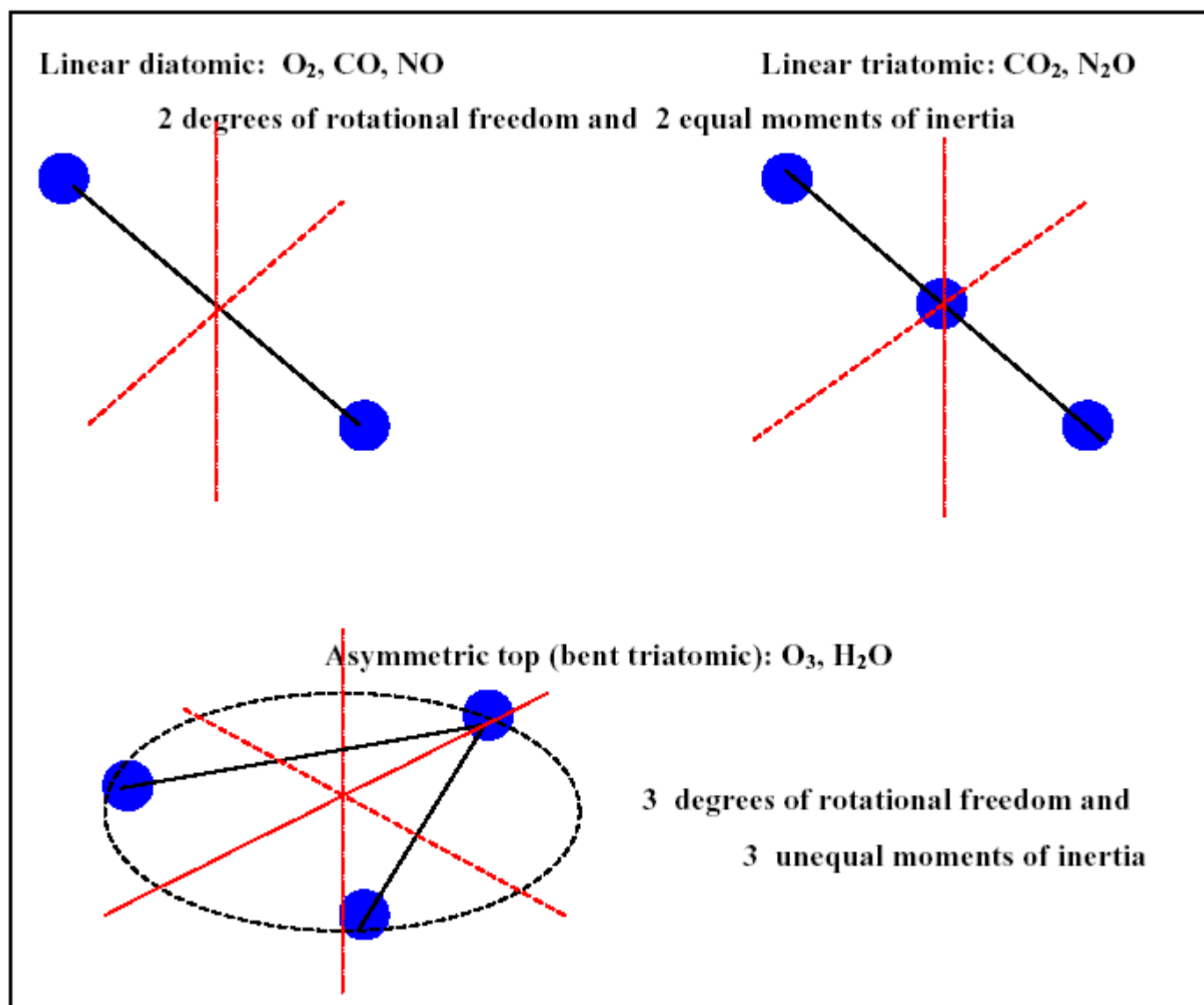
NOTE: Both H_2O and O_3 have three normal band ν_1 , ν_2 and ν_3 : all are optically active.

NOTE: CH_4 has nine normal modes but only ν_3 and ν_4 are active in IR.

5) Rotational –vibrational transitions:

Pure rotational transitions can be understood by evoking the notion of a rigid quantized rotator.

Figure 6.6 Axes of rotational freedom for linear and asymmetric top molecules.



Pure rotational transitions.

Let's consider a diatomic molecule with masses m_1 and m_2 at distances r_1 and r_2 from their common center of gravity. The moment of inertia of this two-mass rigid rotator is

$$I_m = m_1 r_1^2 + m_2 r_2^2$$

If r is the distance between the atoms, we have

$$r_1 = \frac{m_2}{m_1 + m_2} r \quad \text{and} \quad r_2 = \frac{m_1}{m_1 + m_2} r$$

Introducing the reduced mass m' as

$$m' = \frac{m_1 m_2}{m_1 + m_2}$$

we have
$$I_m = \frac{m_1 m_2}{m_1 + m_2} r^2 = m' r^2$$

The angular momentum L of a rigid rotator is defined as

$$L = I_m \omega = m' r^2 \omega$$

where ω is the angular velocity (rad sec^{-1})

The kinetic energy of a rotator is equal

$$E_{rot} = \frac{1}{2} L \omega = \frac{1}{2} I_m \omega^2$$

Classic rotator: both angular momentum and rotational kinetic energy are continuous

Quantized rotator: Quantum restrictions on rotational energy as a consequence of the quantum restrictions on angular momentum (which found from a solution of the Schroedinger equation).

The quantum restrictions on angular momentum are
(photon has angular momentum $h/2\pi$):

$$I_m \omega = \frac{h}{2\pi} [J(J+1)]^{1/2}$$

J is the **rotational quantum number**; $J = 0, 1, 2, 3, \dots$

h is the Planck's constant.

Thus we have

$$E_{rot} = \frac{1}{2} I_m \omega^2 = \frac{1}{2} \frac{(I_m \omega)^2}{I_m} = \frac{h^2}{8\pi^2 I_m} J(J+1)$$

or

$$\boxed{E_J = B h c J (J+1)} \quad [6.3]$$

B is the rotational constant and it depends on the moments of inertia ***I_m*** of a given molecule as

$$B = \frac{h}{8\pi^2 c I_m}$$

Units of B: LENGTH⁻¹

Selection rules: $\Delta J = 1$ for absorption and $\Delta J = -1$ for emission

Consider rotational transition between the upper energy level E' and lower energy level E'' . We have for upper level $E' = B h c J' (J'+1)$ and for lower level $E'' = B h c J'' (J''+1)$. Thus

$$\Delta E_j = E' - E'' = 2Bhc(J''+1) = 2BhcJ', J' = J''+1$$

Recalling that $\Delta E_j = \nu h c$, position of a pure rotational line is given by

$$\boxed{\nu = 2 B J'} \quad (\text{cm}^{-1})$$

=> equally spaced lines because B is constant for a given molecule

NOTE: The nonlinear molecules H_2O and O_3 , asymmetric tops with three moments of inertia, give very complex spectra.

Example: Assume a rotational constant of $B = 2.0 \text{ cm}^{-1}$. Say a photon is absorbed in a rotational transition from $J = 7$ to $J = 8$. The rotational energy levels are $E_J = 56Bhc \rightarrow E_J = 72Bhc$ and the change in energy levels is $\Delta E = 16Bhc$ for a wavenumber of $\nu = 16B = 32 \text{ cm}^{-1}$.

Pure vibrational transitions.

Pure vibrational energy:

Similar to the derivation above, one can introduce a classical vibrator (whose energies are continuous) and then apply the quantum restrictions from the Schroedinger equation.

The allowed energy levels are

$$E_{v_k} = h c \nu_k (v_k + 1/2) \quad [6.4]$$

where ν_k is the wavenumber of the k-normal vibrational mode;

v_k is the **vibrational quantum number**; $v_k = 0, 1, 2, 3, \dots$

For pure vibrational transition, we have $\Delta E = h \nu_k$

Vibrating molecule is like quantum mechanical harmonic oscillator:

$$E_n = h\nu = (n + 1/2) \frac{h}{2\pi} \sqrt{\frac{k_{bond}}{m_r}}$$

k_{bond} = spring constant of bond, m_r = reduced mass,

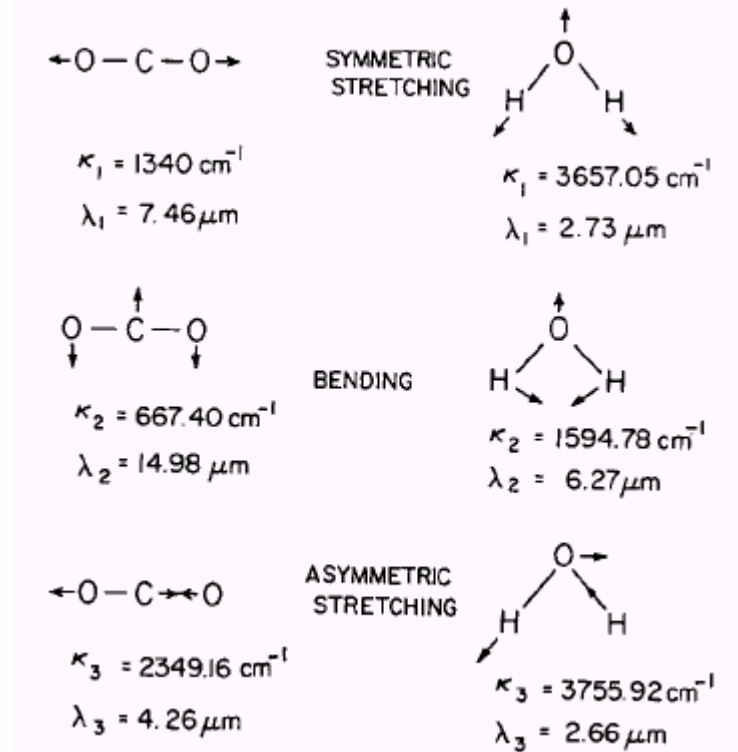
n = vibrational quantum number.

Most infrared absorption bands from the fundamental transition: $n = 0 \rightarrow 1$.

Hot bands are from lower state $n > 0$.

Isotopic bands are from nonstandard isotopes in molecule.

Combination bands are from multiple vibrational mode changes.



Vibrational modes of carbon dioxide and water vapor.

[Kidder and Vonder Haar, Fig. 3.15]

Combined vibrational-rotational transitions

Vibrational transitions include rotational transitions, giving a band of many absorption lines.

$$E_{j,v} = B h c J (J+1) + h c \nu_k (\nu_k + 1/2) \quad [6.5]$$

- Because $E_{vib} > E_{rot}$, the spectrum of the combined transitions is a series of rotational lines grouped around the vibrational wavenumber:

For $\Delta J = +1$ we have $\nu = \nu_k (2B J')$, $J' = 1, 2, 3 \dots$

For $\Delta J = -1$ we have $\nu = \nu_k (-2B (J'+1))$, $J' = 0, 1, 2, 3 \dots$

where J' is the rotational quantum number in the excited vibrational state ν_k ,

Compare rotational and vibrational transitions with thermal energy:

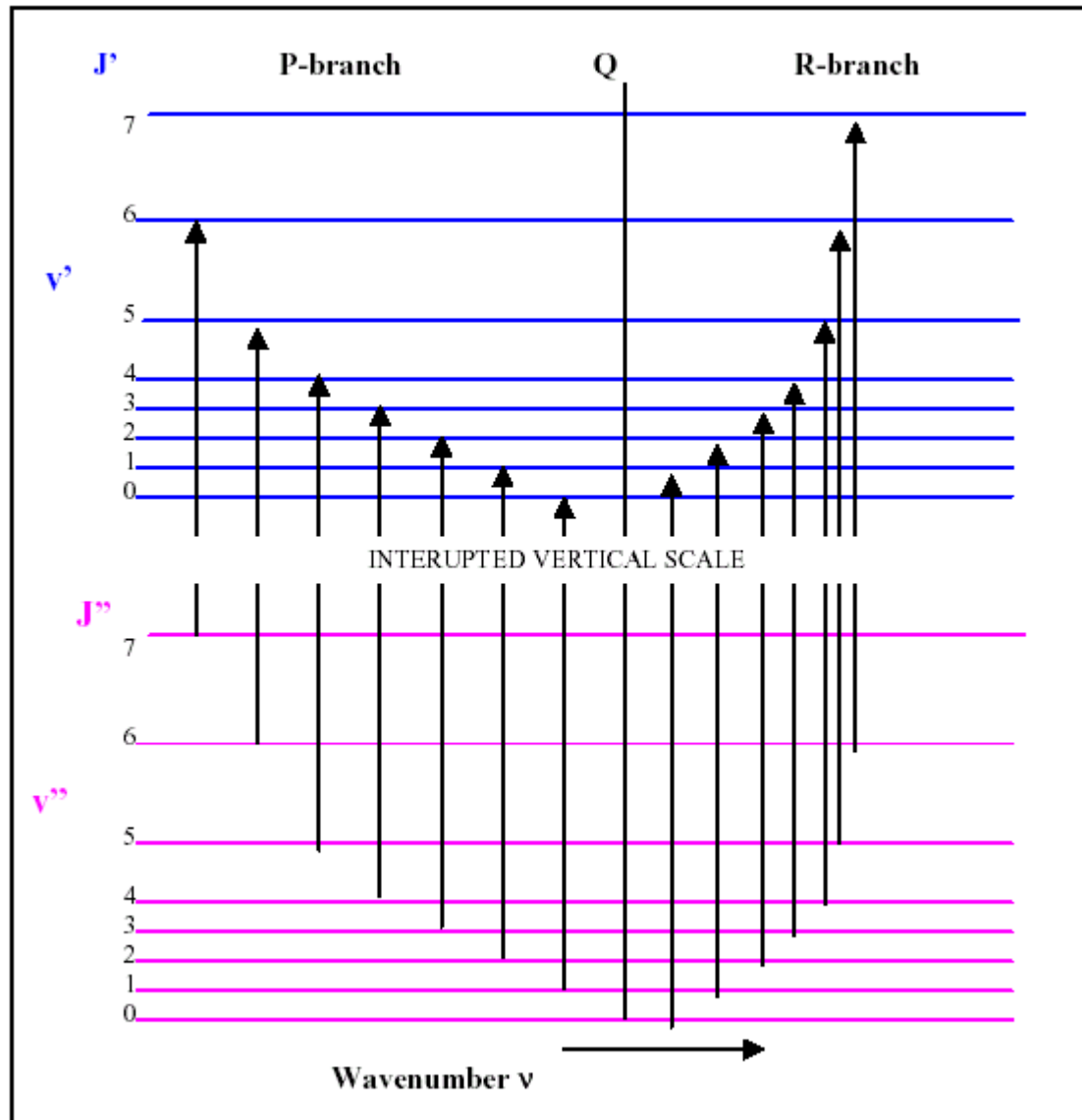
Thermal ($k_B T$): $\nu = k_B T / hc = 250 \text{ K} / 1.44 \text{ K cm} = 175 \text{ cm}^{-1}$

Vibrational transitions: $\sim 600 < \nu < 10000 \text{ cm}^{-1}$

Rotational transitions: $\sim 1 < \nu < 500 \text{ cm}^{-1}$

Molecules in lowest vibrational state, but many rotational states occupied.

Figure 6.6 Simultaneous transitions in vibrational and rotational energies.
 (“ denotes lower energy level and ‘ denotes upper energy level).



**Selection
rules for
rotational
transitions:**

P-branch:

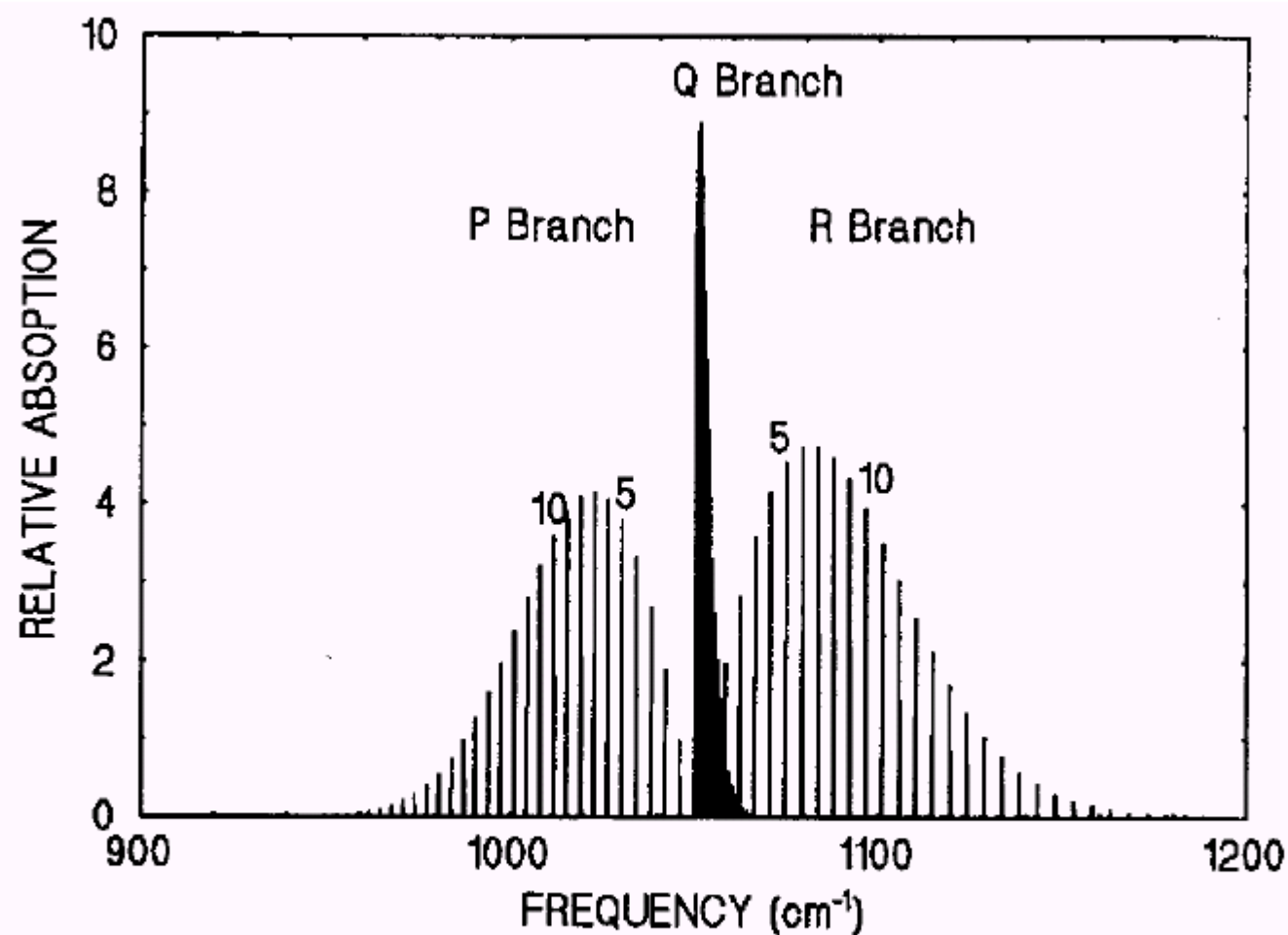
$$\Delta J = -1$$

Q-branch:

$$\Delta J = 0$$

R-branch:

$$\Delta J = +1$$



Simulated high resolution absorption spectrum of a linear molecule. The Q branch ($\Delta J = 0$) is sometimes allowed if there are more than two atoms in the molecule. [Kyle Fig. 9.2]

2. Spectral line shapes: Lorentz profile, Doppler profile, and Voigt profile.

Three main properties that define an absorption line: central position of the line (e.g., the central frequency $\tilde{\nu}_0$ or the central wavenumber ν_0), strength of the line (or intensity, S), and shape factor (or line profile, f) of the line.

$$\tau = k_\nu u \quad k_\nu = S f(\nu - \nu_0) \quad \int f(\nu) d\nu = 1$$

τ is optical depth of layer, u is absorber amount, k_ν is absorption coefficient (e.g. g/cm²), ν_0 is the line center frequency, $f(\nu)$ is the line shape function, and S is the line strength or intensity.

Units: $f(\nu)$ [cm] S [cm/g] or [cm/molec]

Dependencies: $S(T)$ depends on temperature; $f(\nu - \nu_0; \alpha)$ depends on line halfwidth $\alpha(p, T)$, which depends on pressure and temperature.

- Each line has a final width (referred to as **natural broadening of a spectral line**).
- In the atmosphere, several processes may result in an additional broadening of a spectral line of the molecules: 1) collisions between molecules (referred to as the **pressure broadening**); 2) due to the differences in the molecule thermal velocities (referred to as the **Doppler broadening**); and 3) the combination of the above processes.

Lorentz profile of a spectral line is used to characterize the **pressure broadening** and is defined as:

$$f_L(\nu - \nu_0) = \frac{\alpha / \pi}{(\nu - \nu_0)^2 + \alpha^2} \quad [6.6]$$

where $f(\nu - \nu_0)$ is the shape factor of a spectral line;

ν_0 is the wavenumber of a central position of a line;

α is the half-width of a line at the half maximum (in cm^{-1}), (often called the **line width**)

- The **half-width** of the Lorentz line shape is a function of pressure P and temperature T and can be expressed as

$$\alpha(P, T) = \alpha_0 \frac{P}{P_0} \left(\frac{T_0}{T} \right)^n$$

where α_0 is the reference half-width for STP: $T_0 = 273\text{K}$; $P = 1013 \text{ mb}$.

α_0 is in the range from **about 0.01 to 0.1 cm^{-1}** for most atmospheric radiatively active gases.

For most gases $n = 1/2$

NOTE: The above **dependence on pressure** is very important because atmospheric pressure varies by an order of 3 from the surface to about 40 km.

- The **Lorentz profile** is fundamental in the radiative transfer in the lower atmosphere where the pressure is high.
- The collisions between like molecules (**self-broadening**) produces the large line-widths than do collisions between unlike molecules (**foreign broadening**). Because radiatively active gases have low concentrations, the **foreign broadening** often dominates in infrared radiative transfer.

Doppler profile is defined in the absence of collision effects (i.e., pressure broadening) as:

$$f_D(\nu - \nu_0) = \frac{1}{\alpha_D \sqrt{\pi}} \exp \left[- \left(\frac{\nu - \nu_0}{\alpha_D} \right)^2 \right] \quad [6.7]$$

α_D is the **Doppler line width**

$$\alpha_D = \frac{V_0}{c} (2k_B T / m)^{1/2}$$

where c is the speed of light; k_B is the Boltzmann's constant, m is the mass of the molecule.

The Doppler half-width at the half maximum is $\alpha_D (1n2)^{1/2}$

NOTE: The Doppler effect comes from random molecular motions. If the molecule moves with the thermal velocity V and emits at the frequency $\tilde{\nu}_0$, it would appear that it

emits at the frequency $\tilde{\nu} = \tilde{\nu}_0 \left(1 \pm \frac{V}{c} \right)$, where c is the speed of light and $V \ll c$.

- The Doppler broadening is important at the altitudes from about 20 to 50 km.

Voigt profile is the combination of the Lorentz and Doppler profiles to characterize broadening under the low-pressure conditions (above about 40 km in the atmosphere). (i.e., it is required because the collisions (pressure broadening) and Doppler effect can not be treated as completely independent processes:

$$f_{Voigt}(\nu - \nu_0) = \int_{-\infty}^{\infty} f_L(\nu' - \nu_0) f_D(\nu - \nu') d\nu' =$$

$$\frac{\alpha}{\alpha_D \pi^{3/2}} \int_{-\infty}^{\infty} \frac{1}{(\nu' - \nu_0')^2 + \alpha^2} \exp \left[- \left(\frac{\nu - \nu'}{\alpha_D} \right)^2 \right] d\nu' \quad [6.8]$$

NOTE: The Voigt profile requires numerical calculations.

Nature of the Voigt profile:

- At high pressure: the Doppler profile is narrow compare to the Lorentz profile so under these conditions the Voigt profile is the same as Lorentz profile.
- At low pressure: the behavior is more complicated – a kind of hybrid line with a Doppler center but with Lorentz wings.